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DESIGNATED/ELECTED OFFICE (DO/EO/US)  
CONCERNING A FILING UNDER 35 U.S.C. 371**

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INTERNATIONAL APPLICATION NO.

**PCT/JP97/04848**

INTERNATIONAL FILING DATE

**25 DECEMBER 1997**

[EARLIEST] PRIORITY DATE CLAIMED

**26 DECEMBER 1996**

TITLE OF INVENTION

**ELECTROSTATICALLY CHARGED IMAGE DEVELOPING TONER  
CONTAINING A POLYOLEFIN RESIN HAVING A CYCLIC STRUCTURE**

APPLICANTS FOR DO/EO/US

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Applicants herewith submit to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☒ is transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ has been transmitted by the International Bureau.
  - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ A translation of the International Application into English (35 U.S.C. 371(c)(2)), including 0 sheets of formal drawings and a copy of the International Search Report.
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
  - b. ☐ have been transmitted by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☐ An oath or declaration of the inventors (35 U.S.C. 371(c)(4)).
10. ☐ The annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

**Items 11. to 16. below concern other document(s) or information included:**

11. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☒ A FIRST preliminary amendment.  
☐ A SECOND or SUBSEQUENT preliminary amendment.

14. ☐ A substitute specification.

15. ☐ A change of power of attorney and/or address letter.

16. ☒ Other items or information:

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PCT/JP97/04848

ATTORNEY'S DOCKET NO.

514425-3732

24 JUN 1999

17. ☒ The following fees are submitted:

(CALCULATIONS /PTO USE ONLY)

**Basic National Fee (37 CFR 1.492(a)(1)-(5):**

Search Report has been prepared by the EPO or JPO.....\$840.00(\$840.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) ( .....\$700.00

No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2))...\$770.00(

Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO.....\$1040.00

International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4).....\$96.00

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Multiple dependent claim(s) (if applicable) /+ \$210.00 (\$ /

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NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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WILLIAM F. LAWRENCE  
NAMEDated: JUNE 24, 199928,029  
REGISTRATION NUMBER

PATENT  
514425-3732

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants : NISHIOKA et al.  
U.S. Serial No. :  
Priority Appln. : PCT/JP97/04848  
Priority Filing Date : 25 December 1997  
For : **ELECTROSTATICALLY CHARGED  
IMAGE DEVELOPING TONER  
CONTAINING A POLYOLEFIN RESIN  
HAVING A CYCLIC STRUCTURE**

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New York, NY 10151  
June 24, 1999

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PRELIMINARY AMENDMENT

Assistant Commissioner for Patents  
Washington, D.C. 20231

ATTN: Box Patent Application

Sir:

Preliminary to the examination of this U.S. National  
Phase application, please enter the following amendments:

IN THE CLAIMS:

Claim 3, line 2, delete "or 2";

Claim 5, line 2, delete "any one of claims 1 to 4" and

insert --claim 1--;

Claim 6, line 2, delete "any one of claims 1 to 4" and  
insert --claim 1--;

Claim 8, line 2, delete "any one of claims 1 to 7" and  
insert --claim 1--;

Claim 10, line 2, delete "any one of claims 1 to 7" and  
insert --claim 1--;

Claim 12, line 2, delete "any one of claims 1 to 11"  
and insert --claim 1--;


REMARKS

This application includes a multiply dependent claims.  
The amendment removes the multiple claim dependencies, and the  
filing fee for this application was computed on the basis that no  
dependent claim depends from more than one preceding claim.

Entry of this amendment and an early examination on the  
merits are respectfully solicited.

Respectfully submitted,  
FROMMER LAWRENCE & HAUG LLP

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WFL\jm

TONER FOR DEVELOPMENT OF ELECTROSTATICALLY CHARGED IMAGE  
CONTAINING POLYOLEFIN RESIN HAVING CYCLIC STRUCTURE

FIELD OF THE INVENTION

The present invention relates to a toner for development of an electrostatically charged image. More specifically, this invention relates to a dry one-component magnetic toner, a dry one-component nonmagnetic toner, a dry two-component toner, a dry polymerized toner, a liquid dried toner, or a liquid toner which, when fixed, is excellent in anti-spent toner effect, and can form a well fixed, highly transparent, sharp image.

The invention also relates to the above-mentioned toner for use in copiers, printers, facsimile machines, color copiers, color laser copiers, color laser printers, and electrophotographic high speed printers.

BACKGROUND OF THE INVENTION

Electrostatically charged image developing copiers and printers are gaining popularity because of widespread office automation. With this background, demand is growing for high grade or sharp copied images which are highly light transmissive and well fixed.

Under these circumstances, we stated to the following effect in Japanese Patent Application No. 354063/95 (filed December 29, 1995), which was not laid open to the public when the present application was filed: "The relevant problem can be solved or diminished by using a polyolefin resin having a cyclic structure as a binder resin for a toner for heat roller fixing type electrostatically charged image

developing copiers and printers, and also by incorporating less than 50% by weight of the polyolefin resin with a high viscosity into the entire binder resin. As a result, a sharp, high quality copied image which is excellent in fixing, light transmission and anti-spent toner effect can be obtained. Particularly when this resin is used in a color toner, its characteristics are exhibited."

This previous invention, however, was defective in that it was difficult to get a sufficiently broad offset-free temperature range suitable for practical use, and scarcely achieved an enough fixing property at an even higher copying speed to meet users' requirement.

In fixing a toner image onto plain paper or an OHP film, various fixing methods are available, such as hot roller fixing, hot belt fixing, pressure fixing, radiant heat fixing, or flash fixing. In recent years, energy saving symbolized by "Energystar restriction" has been demanded increasingly, and demand has become intense for a toner fixable at a low temperature and a low pressure. The thermal properties and mechanical properties of conventional styrene-acrylate resins and polyester resins, or the polyolefin resins having a cyclic structure described in Japanese Patent Application No. 354063/95 cannot satisfy the requirements at lower temperatures or pressures than the current level. Improvement in the thermal properties of these resins on one hand resulted in the deterioration of storage stability of the toner on the other hand.

General formulations for toners in electrostatically charged image developing copiers and printers are shown in Table 1.

Table 1 General Formulations of Toners

(Unit: % by weight)

	Binder resin	Colorant	Charge control agent	Function imparting agent	Magnetic powder	Solvent
Dry two-component toner	50-100	0-20	0-10	0-20	-	-
Dry nonmagnetic one-component toner	50-100	0-20	0-10	0-20	-	-
Dry magnetic one-component toner	0-100	0-20	0-10	0-20	0-60	-
Dry polymerized toner	50-100	0-20	0-10	0-20	-	-
Liquid dried toner	15-50	0-10	0-5	0-10	-	50-70
Liquid toner	15-50	0-10	0-5	0-10	-	50-70

The object of the present invention is to provide a toner in a dry two-component, dry nonmagnetic one-component, dry magnetic one-component, dry polymerized, liquid dried, or liquid toner developer which exhibits the effects achieved by Japanese Patent Application No. 354063/95, is to propose a sufficiently broad offset-free temperature range suitable for practical use, can attain sufficient fixing property even by high speed copying, and gives a higher grade image, namely, good in fixing, highly optically transparent, sharp image in an electrostatically charged image developing copier or printer.

#### DISCLOSURE OF THE INVENTION

The foregoing object is attained by using as a binder resin for a toner a binder resin which at least contains a polyolefin resin having a cyclic structure, the polyolefin resin having a cyclic structure comprising a resin or resin fraction having a number average molecular weight ( $M_n$ ), as measured by GPC, of less than 7,500 and a resin or resin fraction having said number average molecular weight of 7,500 or more; and in which in said polyolefin resin having a cyclic structure, a resin or resin fraction having an intrinsic viscosity (i.v.) of 0.25 dl/g or more, a heat distortion temperature (HDT) by the DIN 53461-B method of 70°C or higher, and a number average molecular weight ( $M_n$ ) of 7,500 or more and a weight average molecular weight ( $M_w$ ) of 15,000 or more, as measured by the GPC method, is contained in a proportion of less than 50% by weight based on the entire binder resin.

Thus, the invention concerns a toner for development



of an electrostatically charged image, the toner consisting essentially of a binder resin, a colorant, a function imparting agent (generally, wax as a mold release agent), and a charge control agent, the binder resin at least containing the above-described polyolefin resin having a cyclic structure, the polyolefin resin satisfying the above conditions.

The polyolefin resin having a cyclic structure used herein is, for example, a copolymer of an  $\alpha$ -olefin (broadly, an acyclic olefin), such as ethylene, propylene or butylene, with a cyclic and/or polycyclic compound having at least one double bond, such as cyclohexene or norbornene tetracyclododecene (TCD) and dicyclopentadiene (DCPD), the copolymer being colorless and transparent, and having high light transmission. This polyolefin resin having a cyclic structure is a polymer obtained, for instance, by a polymerization method using a metallocene catalyst or a Ziegler catalyst and catalyst for the metathesis polymerization, therefore double-bond-opening and ring-opening polymerization reactions.

Examples of synthesis of the polyolefin resin having a cyclic structure are disclosed in JP-A-339327/93, JP-A-9223/93, JP-A-271628/94, EP-A-203799, EP-A-407870, EP-A-283164, EP-A-156464 and JP-A-253315/95.

According to these examples, the polyolefin resin is obtained by polymerizing optionally one acyclic olefin monomer with at least one cycloolefin monomer at a temperature of -78 to 150°C, preferably 20 to 80°C, and a pressure of 0.01 to 64 bars in the presence of a catalyst comprising at least one metallocene containing zirconium or hafnium together with

a cocatalyst such as aluminoxane. Other useful polymers are described in EP-A-317262, hydrogenated polymers and copolymers of styrene and dicyclopentadiene are useful too.

When dissolved in an inert hydrocarbon such as an aliphatic or aromatic hydrocarbon, the metallocene catalyst is activated. Thus, the metallocene catalyst is dissolved, for example, in toluene for preliminary activation and reaction in the solvent.

The important properties of COC are softening point, melting point, viscosity, dielectric properties, anti off set window and transparency. These properties can be adjusted advantageously by selecting ratio of monomers/comonomers, ratio of comonomers in copolymer, molecular weight, molecular weight distribution, hybrid polymers, blends and additives.

The molar ratio of the acyclic olefin and the cycloolefin charged for the reaction can be varied widely depending on the targeted polyolefin resin having a cyclic structure. This ratio is adjusted, preferably, to 50:1 to 1:50, more preferably 20:1 to 1:20.

When the copolymer components charged for the reaction are a total of two compounds, ethylene as the acyclic polyolefin and norbornene as the cycloolefin, the glass transition point ( $T_g$ ) of the cyclic polyolefin resin as the reaction product is influenced greatly by their charge proportions. When content of norbornene is increased, the  $T_g$  also tends to rise. When the proportion of norbornene charged is approximately 60% by weight, for instance, the  $T_g$  is about 60 to 70°C.

The physical properties, such as number average

molecular weight are controlled as known from the literatures.

The colorless, transparent, highly light-transmissive polyolefin having a cyclic structure used in the present invention may be a mixture of a low-viscosity resin having a number average molecular weight, as measured by GPC, of less than 7,500, preferably 1,000 to less than 7,500, more preferably 3,000 to less than 7,500, a weight average molecular weight, as measured by GPC, of less than 15,000, preferably 1,000 to less than 15,000, more preferably 4,000 to less than 15,000, an intrinsic viscosity (i.v.) of less than 0.25 dl/g, Tg of preferably lower than 70°C, and a high-viscosity resin having a number average molecular weight, as measured by GPC, of 7,500 or more, preferably 7,500 to 50,000, a weight average molecular weight, as measured by GPC, of 15,000 or more, preferably 50,000 to 500,000, an i.v. of 0.25 dl/g or more. Alternatively, the polyolefin resin may have a molecular weight distribution with a single peak, and contain a resin fraction having a number average molecular weight of less than 7,500 and a resin fraction having a number average molecular weight of 7,500 or more. Alternatively, the polyolefin resin may have two or more peaks, in which its resin fraction having at least one of these peaks has a number average molecular weight of less than 7,500 and its resin fraction having the other peak has a number average molecular weight of 7,500 or more. The resin fractions mentioned here refer to respective resin components before mixing if the polyolefin resin having a cyclic structure is composed of a mixture of different components, such as those with various number average

molecular weights; otherwise it refers to resin divisions formed by fractionating the final synthetic product by suitable means such as GPC. If these resin fractions are monodisperse or close to monodisperse,  $M_n$  of 7,500 nearly corresponds to  $M_w$  of 15,000.

The high-molecular weight/low-molecular weight polyolefin resin having a cyclic structure has the above-mentioned number average molecular weights  $M_n$ , weight average molecular weights  $M_w$ , intrinsic viscosities i.v. Thus, the  $M_w/M_n$  ratio, used as a measure of the degree of dispersion of molecular weight distribution, is as low as from 1 to 2.5, namely, a monodisperse or nearly monodisperse state. Thus, a toner having a quick heat response and a high fixing strength can be produced. This polyolefin resin not only enables fixing at a low temperature and a low pressure, but also contributes to the storage stability, anti-spent toner effect, and electric stability properties such as uniform charge distribution or constant charging efficiency or charge elimination efficiency. If the low viscosity resin, in particular, is monodisperse or nearly monodisperse, the resulting toner shows better heat response characteristics, such as instantaneous melting or setting behavior.

The high-viscosity/low-viscosity polyolefin resin having a cyclic structure, moreover, is colorless, transparent, and highly light-transmissive. For instance, the azo pigment Permanent Rubin F6B (Hoechst AG) was added to the resin, and the mixture was thoroughly kneaded, and then formed into a sheet by means of a press. This sheet was confirmed to be highly transparent. Thus, the resin is sufficiently usable for a color toner. Measurement by the

DSC method has shown this polyolefin resin to require a very low heat of fusion. Hence, this resin can be expected to markedly reduce energy consumption for fixing.

The high-viscosity polyolefin resin having a cyclic structure also has the above-mentioned properties; thus, as contrasted with the low-viscosity polyolefin resin, it imparts structural viscosity to the toner, thereby improving the offset preventing effect and the adhesion to a copying medium such as paper or film.

If the amount of the high-viscosity resin used is 50% by weight or more based on the entire binder resin, the uniform kneading properties extremely decline, impeding the toner performance. That is, a high grade image, i.e., a sharp image with high fixing strength and excellent heat response, cannot be obtained.

The toner for development of an electrostatically charged image according to the present invention has the binder resin at least containing the polyolefin resin having a cyclic structure, in which the polyolefin resins having low viscosity and high viscosity are used as the polyolefin resin. Hence, the offset-free temperature range covers the high temperature side and the low temperature side, the fixing properties by high speed copying are enhanced, and the fixing properties at low temperatures and low pressures are both improved.

To broaden the offset-free temperature range to the low temperature side, the low viscosity polyolefin resin with a number average molecular weight of less than 7,500 contributes. To broaden the offset-free temperature range to the high temperature side, on the other hand, the high

viscosity polyolefin resin with a number average molecular weight of 7,500 or more contributes. In order to broaden the offset-free temperature range to the high temperature side more effectively, it is preferred for the high viscosity polyolefin resin with a number average molecular weight of 20,000 or more to be present. The proportions of the cyclic structure polyolefin resins with number average molecular weights of less than 7,500 and 7,500 or more contained in the entire binder resin are each preferably 0.5 part by weight or more, more preferably 5 parts by weight or more, based on 100 parts by weight of the entire binder resin. If the content of each polyolefin resin is less than 0.5 part by weight, it is difficult to obtain a practical broad offset-free temperature range.

In the case of the polyolefin resin having a cyclic structure composed of the low viscosity polyolefin resin with a number average molecular weight of less than 7,500 and the high viscosity polyolefin resin with a number average molecular weight of 25,000 or more, a medium viscosity polyolefin resin having a cyclic structure with a number average molecular weight of 7,500 or more but less than 25,000 is added to enhance the compatibility of these low and high viscosity polyolefin resin components. This addition has been found effective in bringing an offset-free range continuously.

In other words, the binder resin at least containing a polyolefin resin having a cyclic structure, the polyolefin resin comprising resins or resin fractions having three molecular weight ranges expressed by number average molecular weight ( $M_n$ ), as measured by GPC, of less than 7,500,

7,500 or more but less than 25,000, and 25,000 or more is also an advantageous embodiment of the present invention. The resin fractions constituting the respective molecular weight ranges may be a resin having a molecular weight distribution with one or two peaks that can be divided into fractions with the above three molecular weight ranges expressed as Mn. Alternatively, the resin fractions constituting the respective molecular weight ranges may be a mixture of resins having molecular weight distributions with three or more peaks that have at least one molecular weight peak in each of the above molecular weight ranges.

The proportion of the medium viscosity polyolefin resin or resin fraction for increasing compatibility is preferably 1 part by weight or more, more preferably 5 parts by weight or more, based on 100 parts by weight of the entire binder resin.

In the present invention, a toner using as a binder resin a mixture of the polyolefin resin, composed of resins or resin fractions with Mn of less than 7,500 and Mn of 7,500 or more, and other resin also realizes a high grade image, i.e., a high fixing strength and sharp image. The other resin refers to one of a polyester resin, an epoxy resin, a polyolefin resin, a vinyl acetate resin, a vinyl acetate copolymer resin, a styrene-acrylate resin and other acrylate resin, or a mixture or a hybrid polymers of any of the mentioned polymers. The proportions of the polyolefin resin having a cyclic structure and the other resin used in the binder resin are 1 to 100, preferably 20 to 90, more preferably 50 to 90 parts by weight of the former, and 99 to 0, preferably 80 to 10, more preferably 50 to 10 parts

by weight of the latter, based on 100 parts by weight of the binder resin. If the amount of the former resin is less than 1 part by weight, it becomes difficult to obtain a high grade image.

By introducing carboxyl groups into the polyolefin resin having a cyclic structure, its compatibility with the other resin and the dispersibility of the pigment can be improved. Furthermore, the adhesion to paper or film, a copying medium, can be enhanced, leading to increased fixability. Two-stage reaction method of polymerizing the polyolefin resin having a cyclic structure first, and introducing carboxyl groups subsequently is preferred.

At least two methods are available for introducing the carboxyl groups into the resin. One is a method of oxidizing an alkyl group, such as methyl, at the end of the resin by the fusing air oxidation method to convert it into a carboxyl group. With this method, however, the polyolefin resin of a cyclic structure that has been synthesized using a metallocene catalyst has few branches, making it difficult to introduce many carboxyl groups into this resin. The other method is to add a peroxide to the resin, and react maleic anhydride or other ester and ester derivatives, amides and other polar unsaturated compounds with the resulting radical portion. With this method, it is theoretically possible to introduce many carboxyl groups onto the resin, but an increased proportion of introduction results in yellowing of the resin, making its transparency poor. If the use of the product is restricted to a toner, therefore, it is preferred to introduce 1 to 15% by weight, based on the resin, of maleic anhydride. The same improvement can be achieved



by introducing hydroxyl groups or amino groups by a known method.

To improve the Fixing-ability of the toner, a crosslinked structure may be introduced into the polyolefin resin having a cyclic structure. One of the methods for introducing this crosslinked structure is to add a diene monomer, such as norbornadiene or cyclohexadiene, together with the acyclic olefin and the cycloolefin, followed by reacting the system, thereby obtaining a terpolymeric polyolefin having a cyclic structure. As a result of this method, the resin has a terminal showing activity even without a crosslinking agent. A known chemical reaction such as oxidation or epoxidation, or the addition of a crosslinking agent to form a crosslinked structure, results in the functioning of the resin.

Another method is to add a metal such as zinc, copper or calcium to the polyolefin resin of a cyclic structure having carboxyl groups introduced therein, and then blend and melt the mixture with a screw or the like to disperse the metal uniformly as fine particles in the resin, thereby forming an ionomer having a crosslinked structure.

Concerning a technology itself on such an ionomer, United States Patent No. 4,693,941, for example, discloses a terpolymer of ethylene containing carboxyl groups which may take the form of a divalent metal salt upon partial or complete neutralization in an attempt to obtain toughness.

JP-A-500348/94 reports a polyester resin molded product containing an ionomer of an unsaturated carboxylic acid that has about 20 to 80% of the carboxylic acid groups neutralized with zinc, cobalt, nickel, aluminum or copper (II), the product intended for the same purpose.

The toner of the present invention uses a known function imparting agent to enhance the offset preventing effect. To improve this performance further, the addition of wax has been found effective. As a polar wax, at least one wax selected from amide wax, carnauba wax, higher fatty acids and their esters, higher fatty acid metallic soaps, partially saponified higher fatty acid esters, and higher aliphatic alcohols can be used as the function imparting agent. As a nonpolar wax, at least one wax selected from polyolefin wax and paraffin wax can be used as the function imparting agent.

The polar wax may work as an external lubricant for the polyolefin resin which is a nonpolar resin, because of the difference in polarity. The nonpolar wax may work as an external lubricant mainly because of easy surface migration due to its low molecular weight, contributing to improved offset-free properties.

The toner for development of an electrostatically charged image according to the present invention can be obtained by adding a colorant, a charge control agent, a function imparting agent, and if desired, other additives to the aforementioned binder resin, and performing known methods such as extrusion, kneading, grinding and classification. A flowing agent and a lubricant are further added.

The colorant may be a known one, such as carbon black, diazo yellow, phthalocyanine blue, quinacridone, carmine 6B, monoazo red or perylene.

Examples of the charge control agent are known ones such as Nigrosine dyes, fatty acid modified Nigrosine dyes,

metallized Nigrosine dyes, metallized fatty acid modified Nigrosine dyes, chromium complexes of 3,5-di-tert-butylsalicylic acid, quaternary ammonium salts, triphenylmethane dyes, and azochromium complexes.

To the toner of the present invention, there may be further added a flowing agent such as colloidal silica, aluminum oxide or titanium oxide, and a lubricant comprising a fatty acid metal salt such as barium stearate, calcium stearate or barium laurate.

The toner of the present invention can be used as a dry one-component magnetic toner, a dry one-component nonmagnetic toner, a dry two-component toner, a dry polymerized toner, a liquid dried toner, or a liquid toner. This invention is applicable to a copier, a printer, a facsimile machine and an electrophotographic high speed printer. The invention is also applicable as a full-color toner in a color copier, a color laser copier and a color laser printer.

#### EXAMPLES

The present invention will be described in more detail by reference to Examples and Comparative Examples.

The physical properties of the polyolefin resin having a cyclic structure used in the invention are measured by the following methods:

#### GPC conditions for measurement of molecular weight

Molecular weight conversion method:

Standard polyethylene is used.

Column used: JORDI-SAEULE 500x10 LINEAR

Mobile phase: 1,2-dichlorobenzene (135°C)

(flow rate 0.5 ml/min)

Detector: Differential refractometer

Method for measurement of intrinsic viscosity:

Inherent viscosity at 135°C when 1.0 g of the resin was uniformly dissolved in 100 ml of decalin

<Toner preparation method 1>

Dry nonmagnetic one component system and dry two component system:

One % by weight of a charge control agent (Copy Charge NX, Hoechst AG), 4% by weight of amide wax (BNT, Nippon Seika), 0.5% by weight of aerosol silica (HDK-H2000, Wacker Chemie), 5% by weight of magenta pigment (Permanent Rubin F6B, Hoechst AG) as a colorant, and 89.5% by weight of a binder resin were mixed, and melt kneaded at 130°C by a twin roll. Then, the mixture was cooled to solidification, and coarsely crushed, followed by finely dividing the particles using a jet mill. The resulting fine particles were classified to select particles with an average particle diameter of about 10  $\mu\text{m}$ , thereby preparing a toner.

<Toner preparation method 2>

Dry magnetic one component system:

Forty % by weight of a magnetic powder (BL100, Titanium Industry), 1% by weight of a charge control agent (Copy Charge NX, Hoechst AG), 4% by weight of wax (BNT, Nippon Seika), 0.5% by weight of aerosol silica (HDK-H2000, Wacker Chemie), 2.0% by weight of calcium carbonate (Shiraishi Calcium) as an extender pigment and a structural viscosity improver, and 52.5% by weight of a binder resin were mixed, and melt kneaded at 150°C by a twin roll. Then, the mixture was cooled to coagulation, and coarsely ground, followed by finely dividing the particles using a jet mill. The

resulting fine particles were classified to select particles with an average particle diameter of about 10  $\mu\text{m}$ , thereby preparing a toner.

<Toner preparation method 3>

Dry polymerized system:

One % by weight of a charge control agent (Copy Charge NX, Hoechst AG), 4% by weight of wax (BNT, Nippon Seika), 0.5% by weight of aerosol silica (HDK-H2000, Wacker Chemie), and 5% by weight of magenta pigment (Permanent Rubin F6B, Hoechst AG) as a colorant were mechanically dispersed and mixed in monomer components corresponding to 89.5% by weight of a binder resin at the time of polymerization of the binder resin. The mixture was interfacially polymerized into particles with an average particle diameter of about 10  $\mu\text{m}$ , thereby preparing a toner.

<Toner preparation method 4>

Liquid dried system:

Forty % by weight of the toner obtained with the formulation of the dry polymerized system and 60% by weight of an electrolytic solution (Isopar H, Exxon) were mixed, and kneaded by a sand mill to prepare a toner.

<Toner preparation method 5>

Liquid toner:

Forty % by weight of a mixture consisting of 1 part by weight of carbon black (MA-7, Mitsubishi Chemical Corp.) as a colorant, 0.5 part by weight of a charge control agent (Reflex Blue R51, Hoechst AG), and 98.5 parts by weight of a binder resin was mixed with 60% by weight of an electrolytic solution (Isopar H, Exxon). The mixture was kneaded with a sand mill to prepare a toner.

Table 1

Ex. or Comp. Ex. No.	Toner preparation method	Formulation of binder resin				
		Sample No.	Weight %	Sample No.	Weight %	
Ex. 1	1 and 3	1	89.5	-	-	-
Ex. 2	1 and 3	1	60	2	29.5	29.5
Ex. 3	1 and 3	1	60	7	29.5	29.5
Ex. 4	1 and 3	3	89.5	-	-	-
Ex. 5	1 and 3	3	60	7	29.5	29.5
Ex. 6	1 and 3	5	89.5	-	-	-
Ex. 7	1 and 3	5	60	7	29.5	29.5
Ex. 8	1 and 3	1	60	2	14.5	14.5
				9	15	15
Ex. 9	2	1	52.5	-	-	-
Ex. 10	2	1	30	2	22.5	22.5
Ex. 11	2	1	30	7	22.5	22.5
Ex. 12	2	1	30	8	22.5	22.5
Ex. 13	2	3	52.5	-	-	-
Ex. 14	2	3	30	7	22.5	22.5
Ex. 15	2	3	30	8	22.5	22.5
Ex. 16	2	5	52.5	-	-	-
Ex. 17	2	5	30	7	22.5	22.5
Ex. 18	2	5	30	8	22.5	22.5
Ex. 19	2	1	30	2	11	11
	2			9	11.5	11.5

Table 1 (cont'd)

Ex. or Comp. Ex. No.	Toner preparation method	Formulation of binder resin			
		Sample No.	Weight %	Sample No.	Weight %
Ex. 20	4 and 5	1	39.4	-	-
Ex. 21	4 and 5	1	24	2	15.4
Ex. 22	4 and 5	1	24	7	15.4
Ex. 23	4 and 5	1	24	8	15.4
Ex. 24	4 and 5	3	39.4	-	-
Ex. 25	4 and 5	3	24	7	15.4
Ex. 26	4 and 5	3	24	8	15.4
Ex. 27	4 and 5	5	39.4	-	-
Ex. 28	4 and 5	5	24	7	15.4
Ex. 29	4 and 5	5	24	8	15.4
Ex. 30	4 and 5	1	24	2	7.4
				9	8
Comp. Ex. 1	1 and 3	7	89.5	-	-
Comp. Ex. 2	1 and 3	8	89.5	-	-
Comp. Ex. 3	2	7	52.5	-	-
Comp. Ex. 4	2	8	52.5	-	-
Comp. Ex. 5	4 and 5	7	39.4	-	-
Comp. Ex. 6	4 and 5	8	39.4	-	-

Table 2 shows the fundamental properties of the polyolefin resin having a cyclic structure used in the present invention.



Table 2 Fundamental properties

Sample No.	Name	Mw	Mn	i.v.	HDT	Mw/Mn	Tg
1	MT 845	6250	3350	0.19	<70	1.9	61
2	MT 854	66100	27700	1.39	≥70	2.4	66
3	T-745'-MO	6800	3400	<0.25	<70	2.0	78
5	T-745'-CL	12000	3900	<0.25	<70	3.5	76
7	Tafton NE 2155: Polyester resin, Kao Corp.						
8	MC 100: Styrene acrylate resin, NIPPON CARBIDE INDUSTRIES						
9	MT849	40100	22200	0.7	≥70	1.8	65
10	T-745	7000	3800	0.19	<70	1.8	68

Tg: Glass transition point

Sample No. 1 (MT845), No. 2 (MT854) and No. 9 (MT849) are polyolefin resins having a cyclic structure and having a low viscosity, a high viscosity and a medium viscosity, respectively.

Sample No. 3 (T-745'-MO): Prepared by reacting Sample No. 10 (T-745), a copolymer of ethylene and norbornene, with a peroxide and 7% by weight, based on T-745, of maleic anhydride to introduce carboxyl groups therein.

Sample No. 5 (T-745'-CL): Prepared by neutralizing about 70% of the carboxyl groups of Sample No. 3 (T-745'-MO), which has carboxyl groups introduced therein, with zinc for conversion into an ionomer.

Tafton NE 2155: Tg = 65°C

MC100: Tg = 69°C, Mw = 53000, Mn = 23000, Mw/Mn = 2.3

The toners prepared by the above toner preparation methods 1, 2 and 3 were each placed in a commercially available electrophotographic copier (PC100, Canon Inc.), and subjected to performance test. Then, the toners prepared by the toner preparation methods 4 and 5 were each placed in a commercially available electrophotographic copier (FT400i, Ricoh Co., Ltd.), and subjected to performance test. The results are shown in Table 3.

Table 3

	Fixability 10 copies/min	Image sharpness		Light transmission 624 nm	Anti-spent toner effect	Offset-free properties
		Thin line resolving power	Gray scale			
Ex.1	○	○	○	○	○	△
Ex.2	○	○	○	○	○	○
Ex.3	○	△	△	△	△	△
Ex.4	◎	○	○	○	○	△
Ex.5	◎	○	○	○	○	○
Ex.6	◎	○	○	○	○	○
Ex.7	◎	△	△	△	△	○
Ex.8	◎	○	○	○	○	◎
Ex.9	○	○	○	-	○	△
Ex.10	○	○	○	-	○	○
Ex.11	○	○	○	-	△	△
Ex.12	○	○	○	-	△	△
Ex.13	◎	○	○	-	○	△
Ex.14	◎	○	○	-	○	△
Ex.15	◎	○	○	-	○	△
Ex.16	◎	○	○	-	○	○
Ex.17	◎	○	○	-	△	○
Ex.18	◎	○	○	-	△	○
Ex.19	◎	○	○	○	○	◎
Ex.20	○	○	○	-	○	△



In Examples 1 to 8 and 20 to 30 and Comparative Examples 1, 2, 5 and 6, two methods for toner preparation are employed. However, the toner formulation and the resin structure are common, so that the results on the evaluation items are the same.

#### Evaluation methods and evaluation criteria

##### 1) Fixing-ability

The toners prepared with the respective formulations were each used for copying onto recycled papers at a copying rate of 10 copies/min at a fixing temperature of 110 to 140°C, with the fixing temperature for each copying cycle being raised by 10°C. The resulting copy samples were rubbed 10 times with an eraser by using an abrasion tester of Southerland. The load during the test was 40 g/cm<sup>2</sup>. The tested samples were measured for the printing density using a Macbeth reflection densitometer. The symbol × was assigned when even one of the measured values at the respective temperatures was less than 65%. The symbol Δ was assigned when the measured values at the respective temperatures were 65% or more but less than 75%. The symbol ○ was assigned when the measured values at the respective temperatures were 75% or more but less than 85%. The symbol ◎ was assigned when the measured values at the respective temperatures were 85% or more.

##### 2) Image sharpness

The toners prepared with the respective formulations were each used for copying onto recycled papers. The resulting samples were checked against sample images of Data Quest. The thin line resolving power and gray scale of the copy image were used as bases for evaluation. The symbol

× was assigned for a thin line resolving power of 200 dots/inch or less, △ for a thin line resolving power of 201 to 300 dots/inch, and ○ for a thin line resolving power of 301 dots/inch or more. The ratio of the reflection density of the copy image to the reflection density of the sample image, at each step of the gray scale, was evaluated as × when less than 65%, △ when 65% or more but less than 75%, and ○ when 75% or more.

### 3) Light transmission

The magenta-colored toners prepared with the formulations of the Examples and the Comparative Examples were each used to produce sheet-shaped samples 100 μm thick. The light transmission of each sheet sample was measured using an optical filter having a peak at 624 nm. The light transmittance rate at 624 nm was evaluated as × when less than 8%, △ when 8% or more but less than 11%, and ○ when 11% or more.

### 4) Anti-spent toner effect

The toner described in each of the Examples and the Comparative Examples and a ferrite carrier of Powdertech were put in predetermined amounts into a developer box. After the mixture was agitated and triboelectrically treated for 1 week, 5 g of the toner-deposited carrier was weighed. This toner-deposited carrier was put in soapy water to remove the toner electrostatically adhering to the surface. Only the carrier magnetic powder was withdrawn using a magnet. The magnetic powder was immersed in acetone to dissolve and remove the spent toner fused to the surface. A change in the weight after immersion compared with the weight before immersion was evaluated as ○ when less than 0.2%, △ when

0.2 or more but less than 0.5%, and × when 0.5% or more.

#### 5) Offset-free properties

The toners prepared with the respective formulations were each used for copying onto recycled papers at a copying rate of 10 copies/min at a fixing temperature of 90 to 180°C, with the fixing temperature for each copying cycle being raised by 10°C. The printing density of the non-image areas of the resulting samples was measured using a Macbeth reflection densitometer. The printing density of 0.2 or less (printing density of paper = 0.15) represented an offset-free state. The difference between the upper limit and lower limit temperatures in the offset-free state was evaluated as × when 0°C, △ when 1 to 20°C, ○ when 21 to 40°C, and ◎ when higher than 40°C.

## CLAIMS

1. A toner for development of an electrostatically charged image, said toner comprising a binder resin, a colorant, a function imparting agent, and a charge control agent, wherein said binder resin at least contains a polyolefin resin having a cyclic structure, said polyolefin resin having a cyclic structure is composed of a resin or resin fraction having a number average molecular weight ( $M_n$ ), as measured by GPC, of less than 7,500 and a resin or resin fraction having said number average molecular weight of 7,500 or more, and in said polyolefin resin having a cyclic structure, a resin or resin fraction having an intrinsic viscosity (i.v.) of 0.25 dl/g or more, and a number average molecular weight ( $M_n$ ) of 7,500 or more and a weight average molecular weight ( $M_w$ ) of 15,000 or more, as measured by the GPC method, is contained in a proportion of less than 50% by weight based on the entire binder resin.
2. The toner for development of an electrostatically charged image as claimed in claim 1, wherein said binder resin consists of 1 to 100 parts by weight of said polyolefin resin having a cyclic structure, and 99 to 0 parts by weight of other resin comprising one of a polyester resin, an epoxy resin, a polyolefin resin, a vinyl acetate resin, a vinyl acetate copolymer resin, a styrene-acrylate resin and other acrylate resin, a mixture, hybrid polymers or blends of any of them.
3. The toner for development of an electrostatically charged image as claimed in claim 1 or 2, wherein said polyolefin resin having a cyclic structure has at least one polar functional group.



4. The toner for development of an electrostatically charged image as claimed in claim 3, wherein said polyolefin resin having a cyclic structure has at least one polar functional group selected from a carboxyl group, a hydroxyl group and an amino group.
5. The toner for development of an electrostatically charged image as claimed in any one of claims 1 to 4, wherein said polyolefin resin having a cyclic structure is an ionomer.
6. The toner for development of an electrostatically charged image as claimed in any one of claims 1 to 4, wherein said polyolefin resin having a cyclic structure has a crosslinked structure.
7. The toner for development of an electrostatically charged image as claimed in claim 6, wherein said polyolefin resin having a cyclic structure has a structure crosslinked by a diene, ester, amide, sulfide or ether.
8. The toner for development of an electrostatically charged image as claimed in any one of claims 1 to 7, wherein at least one polar wax is used as the function imparting agent.
9. The toner for development of an electrostatically charged image as claimed in claim 8, wherein at least one polar wax selected from amid wax, carnauba wax, higher fatty acids and their esters, higher fatty acid metallic soaps, partially saponified higher fatty acid esters or higher aliphatic alcohols is used as the function imparting agent.
10. The toner for development of an electrostatically charged image as claimed in any one of claims 1 to 7, wherein at least one nonpolar wax is used as the function imparting

agent.

11. The toner for development of an electrostatically charged image as claimed in claim 10, wherein at least one nonpolar wax selected from polyolefin wax or paraffin wax is used as the function imparting agent.
12. The toner for development of an electrostatically charged image as claimed in any one of claims 1 to 11, wherein said polyolefin resin having a cyclic structure that constitutes said binder resin contains resins or resin fractions having three or more molecular weight ranges expressed by number average molecular weight ( $M_n$ ), as measured by GPC, of less than 7500, 7500 or more but less than 25000, and 25000 or more.
13. Liquid dried system containing 30% by weight to 50% by weight of a dried polymerized system containing 0.5% by weight to 5% by weight of a charge control agent, 1% by weight to 10% by weight of wax, 0.1% by weight to 2% by weight of aerosol silica, 1% by weight to 10% by weight of pigment and 85% by weight to 95% by weight of a binder resin; and 50% by weight to 70% by weight of an electrolytic solution.
14. Liquid toner containing 30% by weight to 50% by weight of a mixture containing 0.5% by weight to 1.5% by weight of carbon black, 0.5% by weight to 1.5% by weight of a charge control agent and 85% by weight to 95% by weight of a binder resin; and 50% by weight to 70% by weight of an electrolytic solution.

# ABSTRACT

A toner for development of an electrostatically charged image, said toner comprising a binder resin, a colorant, a function imparting agent, and a charge control agent, wherein said binder resin at least contains a polyolefin resin having a cyclic structure, said polyolefin resin is composed of a resin or resin fraction having a number average molecular weight ( $M_n$ ), as measured by GPC, of less than 7,500 and a resin or resin fraction having said number average molecular weight of 7,500 or more, and in said polyolefin resin having a cyclic structure, a resin or resin fraction having an intrinsic viscosity (i.v.) of 0.25 dl/g or more, and a number average molecular weight ( $M_n$ ) of 7,500 or more and a weight average molecular weight ( $M_w$ ) of 15,000 or more, as measured by the GPC method, is contained in a proportion of less than 50% by weight based on the entire binder resin.

**COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY**

As below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below, I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

**Electrostatically charged image developing toner containing a polyolefin resin having a cyclic structure**

the specification of which

- is attached hereto
- was filed on December 25, 1997 as International Patent Application PCT/JP97/04848 and including all the amendments through the date hereof.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

**Prior Foreign Application(s) for which Priority is Claimed:**

Japan, 8-348546 of December 26, 1996

And I hereby appoint

William F. Lawrence, Registration No. 28,029, of the firm FROMMER LAWRENCE & HAUG, LLP whose post office address is 745 Fifth Avenue, New York, New York 10151, or their duly appointed associate, my attorneys, with full power of substitution and revocation, to prosecute this application, to make alterations and amendments therein, to file continuation and divisional applications thereof, to receive the Patent, and to transact all business in the Patent and Trademark Office and in the Courts in connection therewith, and specify that all communications about the application are to be directed to the following correspondence address:

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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